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Investigation of the photolysis of the surface-adsorbed HNO₃ by combining laser photolysis with Brewster angle cavity ring-down spectroscopy

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ABSTRACT

We have investigated the photolysis of HNO₃ adsorbed on fused silica surfaces by using excimer laser photolysis at 308 and 351 nm combined with direct probing excited NO₂ product retained on surfaces using Brewster angle cavity ring-down spectroscopy. The sensitivity and the capability of this technique in the study of surface photochemical processes have been demonstrated. The quantum yields of the excited NO₂ produced from the HNO₃ photolysis on surfaces are (1.1 ± 0.2) and (1.0 ± 0.3) at 308 and 351 nm. The disappearance rate of excited NO₂ in the presence of H₂O vapor was measured to be $(2.9 \pm 0.8) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹ at 295 K.

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1. Introduction

Nitric acid (HNO₃), formed in the atmosphere through oxidation [1,2] of NO_x ($NO_x = NO + NO_2$), is removed from the atmosphere mainly by wet and dry deposition [1]. Nitric acid deposited on ground, building, and vegetation surfaces was long thought to be a permanent sink for NO_{x} as the gas phase tropospheric HNO₃ photolysis rate is slow [3,4], and the photolysis rate of adsorbed nitric acid was assumed to be slow. However, field study reported [5] that the photolysis rate for HNO₃ deposited on the ground and vegetation surfaces to form HONO and NO_x was one to two orders of magnitude faster than that in the gas phase. The photolysis of HNO₃ adsorbed on ground surfaces has been proposed as a major daytime source of HONO in low-NO_x environments [5–7]. To elucidate the difference between the nitric acid photolysis rates in the gas phase and on surfaces, the Zhu group recently determined [8,9] the UV absorption cross sections of HNO₃ adsorbed on fused silica surfaces in the 290-365 nm region using Brewster angle cavity ring-down spectroscopy [10]. The surface absorption cross sections of HNO₃ are found to be at least two orders of magnitude higher than the cross section values of the nitric acid vapor, in the wavelength region studied. Our group also investigated [11] the photolysis of HNO₃ in the gas phase at 253 and 295 K, on aluminum surfaces at 253 and 295 K, and on ice films at 253 K by using 308 nm excimer laser photolysis combined with cavity ring-down spectroscopy [12,13]. Formation of $OH + NO_2^*$, where NO₂^{*} represents the electronically excited NO₂, was found to be a predominant photolysis pathway from the gas phase photolysis of HNO₃ at 308 nm. The 308 nm photolysis of HNO₃ adsorbed on

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Al surfaces and on ice films was conducted by photolyzing adsorbed HNO₃ on Al and ice surfaces but there was \sim 1.2 cm distance between Al or ice surfaces and the center of the cell where the probe beam was located. The excited NO₂ formed from the photolysis of the adsorbed HNO₃ needed to desorb from the Al and ice surfaces and travel to the center of the cell to be detected by cavity ring-down spectroscopy. Since the probe beam did not directly interact with either Al or ice surface, and it only monitored excited NO₂ that was diffused into the gas phase and in the probe beam area, the experimental technique and configuration we used in the study of the HNO₃ photolysis on Al or ice surfaces had reduced sensitivity, and we had to use higher HNO₃ pressures (HNO₃ pressures on the order of 0.1-0.5 Torr) in the previous surface photolysis study. As a result, surface photolysis study was not conducted by photolyzing a monolayer or several layers of adsorbed HNO₃ on surfaces.

Despite the recent works by our group, there are still unresolved questions concerning the HNO₃ photolysis on surfaces. For example, (1) Can surface photolysis study be conducted under conditions of monolayer or at most several layers of adsorbed HNO₃? (2) What is the 308 nm photolysis quantum yield of adsorbed HNO₃ on fused silica surface at 295 K? Does surface type affect adsorbed HNO₃ photodissociation quantum yield? (3) How does photolysis quantum yield of surface-adsorbed HNO3 vary with wavelength? In this Letter, we report results obtained by exploring the use of Brewster angle cavity ring-down spectroscopy for direct and time-resolved monitoring of excited NO₂ formed from 308 to 351 nm photolysis of HNO3 molecules adsorbed on fused silica Brewster window surfaces. The approach that we developed has allowed us to directly probe excited NO₂ retained on the surface following the photolysis of adsorbed HNO₃ at close to monolayer condition. The disappearance rates of excited NO₂ (formed from

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Figure 1. Schematics combining excimer laser photolysis with probing surface photolysis products using Brewster angle cavity ring-down spectroscopy.

the 308 nm photolysis of adsorbed HNO_3) in the presence of excess H_2O vapor were also measured.

2. Experimental technique

An excimer laser (Lambda Physik LPX110i) operating at 308 or 351 nm was used to photolyze HNO₃ adsorbed on fused silica Brewster windows, the products formed from the photolysis of adsorbed HNO₃ were then probed by Brewster angle cavity ring-down spectroscopy. A diagram of the experimental setup is shown in Figure 1. The custom stainless-steel cell, with shape of a hollow rectangular prism, was vacuum-sealed by a pair of high-reflectance cavity mirrors at both ends. A plate holding two mutually compensating Brewster windows (1 mm thick) were mounted inside the cell along its main optical axis. Two pairs of fused silica windows were attached to the front and back of the cell for transmission of the photolysis beam. The output from the photolysis laser was split into two beams (by using a 50% reflectance beam splitter) which subsequently entered the reaction cell at 90° angle to the main cell axis through two fused silica windows on the front side, the photolysis beams hit the Brewster windows inside the cell before they exited the cell through two fused silica windows on the back side. The photolysis beams did not interact with cell wall, there was no stray light, and the photolysis beam shapes were the same before and after the cell. The probe laser pulse from a dye laser (Continuum ND6000 with Rhodamine 590 laser dye) pumped by a Nd:YAG laser (Continuum Surelite II), delayed relative to the photolysis laser pulse and used to detect excited NO₂ [11], was introduced into the cell along the main optical axis. The probe laser beam overlapped with the photolysis beams on Brewster windows. A fraction of the probe laser pulse was injected into the cavity through the front mirror, and the intensity decay of this fraction inside the cavity was measured by monitoring the weak transmission of light through the rear mirror, with a photomultiplier tube (PMT). The amplified PMT signal was fitted to a singleexponential decay function, from which the ring-down time constant and the total loss per optical pass was calculated. The surface-study cell is equipped with reagent ports, a pumping port, and pressure measurement port, located on top of the cell. A rectangular viewport, made of transparent plastic and installed on the top, along the main optical path, allowed us to view the photolysis beam. The pressure inside the surface-study cell was measured with an MKS Baratron capacitance monometer.

The inner surfaces of the surface-study cell, and the stainless steel joints on the gas transport line, were treated with halocarbon wax or grease (Series 1500 wax and 25-55 grease, Halocarbon Products Corp.) to minimize decomposition of HNO₃ on cell surfaces and on stainless steel joints.

Since the 308 nm absorption cross section of HNO₃ on fused silica surface [8] $(1.2 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1})$ is 1140 times larger than that in the gas phase [11,14,15] $(1.1 \times 10^{-21} \text{ cm}^2 \text{ molecule}^{-1})$, and since the surface photolysis study was carried out at HNO₃ pressures on the order of tens of mTorr, the absorption of the probe beam at 552.84 nm by the excited NO₂, obtained through measurement of the cavity losses with and without introducing the 308 nm excimer laser beam into the surface study cell should be that resulting from the HNO₃ photolysis on surfaces. A pulse/delay generator was used to vary the delay time between the firing of the photolysis laser and the firing of the probe laser. Only fresh HNO₃ sample was used in the surface photolysis study, the sample was pumped away after averaging results over 20-50 photolysis pulses at a given pressure and delay time. We usually evacuated the cell for several minutes to get rid of residual HNO₃ in the cell and we ensured no degassing of HNO₃ from the cell wall before we added new HNO₃ sample to the surface study cell. All experiments were carried out at an ambient temperature of 295 K, and at a repetition rate of 0.5 Hz.

Purified HNO₃ was prepared by vacuum distillation of a 3:2 mixture of sulfuric acid (98%, Mallinckrodt Baker) and nitric acid (70%, Mallinckrodt Baker) at 273 K into a trap cooled at ethanol/dry ice temperature (195 K) [14]. Repeated distillations were conducted, to purify the sample. To further reduce NO₂ impurity before each experiment, we purged NO₂ from the liquid HNO₃ bubbler, by flowing N₂ carrier gas through the bubbler for about 30 min [16], we then pumped the liquid HNO₃ bubbler for 10 min in the absence of N₂ flow. Previous measurements by our group [8,9] indicate that HNO₃ thus purified has an NO₂ impurity of less than 0.05%.

3. Results and discussion

3.1. Time-resolved study of the photolysis of HNO_3 on fused silica surfaces at 295 K

We investigated the 308 and 351 nm photolysis of HNO₃ adsorbed on fused silica surfaces at 295 K, and we directly probed

for excited NO₂ formed from the HNO₃ photolysis on fused silica surfaces using Brewster angle cavity ring-down spectroscopy. Based upon the previous published results by Goodman et al. [17] that HNO₃ molecularly and reversibly adsorbed on SiO₂ particles, we believe that HNO3 deposited on fused silica surfaces retained its molecular form prior to its photolysis by 308 nm/ 351 nm excimer laser beam. Shown in Figure 2 is a product absorption spectrum in the 551.50-558.00 nm region after the 308 nm photolysis beams stroke on Brewster windows and with 100 mTorr HNO₃ inside the surface study cell. The observation of product absorption in a spectral region that the excited NO₂ exhibits strong absorption [11,18] suggests that the excited NO₂ is a product from the HNO₃ photolysis inside the surface study cell. To find out whether the excited NO₂ absorption resulted from the HNO₃ photolysis in the gas phase or resulted from the photolysis of adsorbed HNO₃ on Brewster windows, we added 100 mTorr of HNO₃ into the surface study cell but removed Brewster windows from the ringdown cavity. We could not detect excited NO₂ absorption after we fired excimer laser at 308 nm, suggesting that the excited NO₂ formed from the HNO₃ photolysis in the gas phase was not detectable at an HNO₃ pressure of 100 mTorr inside the surfacestudy cell. As a result, the excited NO₂ absorption shown in Figure 2 originates from the 308 nm photolysis of adsorbed HNO₃. A similar product absorption spectrum was obtained from the photolysis of adsorbed HNO₃ at 351 nm.

The cavity ring-down spectrometer was tuned to the excited NO_2 absorption maximum at 552.84 nm, and the absorption resulting from the photolysis of adsorbed HNO₃ was measured as a function of time. Shown in Figure 3 is a transient round-trip absorption profile measured at 552.84 nm following the 308 nm photolysis of adsorbed HNO₃ at an HNO₃ pressure of 30 mTorr in the cell (The peak absorption wavelength reported here was obtained with a Continuum Nd:YAG pumped dye laser system which offers wavelength accuracy of 0.05 nm. The peak wavelength of 552.57 nm for the excited NO₂ reported by our group [11] was obtained using a Molectron DL14 dye laser which had lower wavelength accuracy).

The probe laser absorption at 552.84 nm initially increases with delay time, between the firing of the photolysis laser and the probe laser, and reaches a maximum at about 12–15 μ s. It subsequently showed rapid decrease with delay time in the 15–60 μ s range followed by residual low absorption that is nearly independent of time at delay times longer than 60 μ s. Both the excited NO₂ and



Figure 2. Cavity ring-down absorption spectrum of the product in the 551.50– 558.00 nm region, after the 308 nm photolysis of adsorbed HNO₃ at 100 mTorr HNO₃ pressure inside the surface-study cell at 295 K. The spectrum was recorded at a wavelength interval of 0.10 nm. The photolysis/probe laser delay was 15 μ s.



Figure 3. Time profile of the round-trip absorption measured at 552.84 nm following the 308 nm photolysis of HNO_3 adsorbed on fused silica surfaces with 30 mTorr of HNO_3 inside the surface-study cell at 295 K. Circles denote experimental data. Curve shown is the kinetic simulation using the AcuCHEM software. See text for details.

the ground state NO₂ absorb probe laser beam at 552.84 nm with respective absorption cross sections [11] of 9.4×10^{-19} and $8.9 \times 10^{-20} \,\mathrm{cm^2 \,molecule^{-1}}$ in the gas phase at 295 K. In the absence of literature absorption cross sections of the excited NO₂ and the ground-state NO₂ on surfaces at 552.84 nm, we assumed the absorption cross sections of the excited NO₂ and the groundstate NO₂ on surfaces to be similar to their gas phase cross section values at the same wavelength. To find out what can be the maximum difference between the absorption cross section of the ground state NO₂ on fused silica surface versus that in the gas phase, we added NO₂ into the surface-study cell, tuned the ringdown probe beam to NO₂ absorption maximum at 446.10 nm, and measured total absorption as a function of the NO₂ pressure in the surface-study cell. We then removed Brewster windows from the ring-down cavity and determined the probe laser absorption as a function of the NO_2 pressure in the cell. By comparing the absorption of the probe beam in the presence of NO₂ but with and without Brewster windows inside the cavity, we found that the majority of the probe laser absorption resulted from the NO₂ absorption in the gas phase for NO₂ pressures in the mTorr range. We also found that NO₂ had little tendency of sticking on fused silica surfaces at room temperature. The surface absorption cross section of ground state NO2 at 446.10 nm is estimated at most twice its gas phase cross section value at this wavelength.

The following kinetic scheme was used to fit the experimental temporal round-trip absorption profiles at 552.84 nm:

$$NO_2^* - S = NO_2^{\dagger} - S \tag{1}$$

$$NO_2^{\dagger} - S = NO_2 - S \tag{2}$$

$$NO_2 - S = NO_2 + S \tag{3}$$

 $Absorption(t) = 8\sigma_{NO_2^{\dagger},surf} \times [NO_2^{\dagger} - S] + 8\sigma_{NO_2,surf} \times [NO_2 - S] \quad (4)$

where NO₂^{*} – S represents the electronically-excited NO₂ that was generated from the photolysis of adsorbed HNO₃, S represents substrate, NO₂[†] – S represents the surface-bound electronically-excited NO₂ that has undergone some degree of relaxation, NO₂ – S denotes the surface-bound ground state NO₂, NO₂ represents the ground state NO₂ that was desorbed from the surface and escaped from the probe beam area, $\sigma_{\text{NO}_2^{\dagger},\text{surf}}$ and $\sigma_{\text{NO}_2,\text{surf}}$ denote the respective surface absorption cross sections of NO₂[†] and NO₂ at

552.84 nm, $[NO_2^{\dagger} - S]$ and $[NO_2 - S]$ represent the respective concentrations of NO_2^{\dagger} and NO_2 on surfaces. Transient absorption profiles at 552.84 nm from the photolysis of adsorbed HNO₃ at HNO₃ pressures of 10, 20, and 30 mTorr inside the cell were compared with the values calculated by the ACUCHEM simulation program [19]. The vibrational redistribution rate constant of surface-bound electronically-excited $NO_2(k_{NO_2^*-S})$, the quenching rate constant of surface-bound, redistributed electronically-excited $NO_2(k_{NO_2^{\dagger}-S})$, and the desorption rate constant of ground-state NO₂ from the ²surface (k_{NO_2-S}) were used as input parameters. Initial values of $k_{NO_2^*-S}$, $k_{NO_n^{\dagger}-S}$, and k_{NO_2-S} were given to the program, and the simulated absorption profiles were compared with the experimental results. Numerical values of $k_{NO_2^{\dagger}-S}$, $k_{NO_2^{\dagger}-S}$, and k_{NO_2-S} were subsequently adjusted so as to optimize the fit. The following rate constant values are extracted: $k_{\rm NO_2^*-S}$ of $(1.4 \pm 0.3) \times 10^5 \, {\rm s}^{-1}$, $k_{\rm NO_2^*-S}$ of $(7.5 \pm 0.6) \times 10^4 \, {\rm s}^{-1}$, and $k_{\rm NO_2-S}$ of $(7.4 \pm 2.7) \times 10^3 \, {\rm s}^{-1}$ at 295 K. $k_{\rm NO_2^*-S}$ of $1.4 \times 10^5 \, {\rm s}^{-1}$ suggests that the electronically-excited NO_2^2 formed from the adsorbed HNO₃ photolysis gets vibrationally redistributed to lower vibrational levels of electronically-excited NO_2 at time scale on the order of 7 µs on surfaces. The extracted $k_{\rm NO^{1}_{2}-S}$ value corresponds to an electronic quenching lifetime on the order of 13 µs, which is shorter than the literature reported lifetimes [20] for quenching of electronically-excited NO₂ of 55-90 µs in the gas phase. Thus, the relaxation rate for electronically-excited NO₂ adsorbed on surface is faster than that in the gas phase. k_{NO_2-S} of $7.4 \times 10^3 \text{ s}^{-1}$ would correspond to surfacedesorption lifetime for the ground state NO2 on the order of 135 µs (Inclusion of desorption of ground-state NO₂ from surface in the simulation makes the simulated temporal absorption profile and the measured temporal absorption profile agree better at $t > 30 \mu s$). Temporal absorption profiles at 552.84 nm from the photolysis of adsorbed HNO₃ at 10, 20, and 30 mTorr HNO₃ pressures in the cell are well fitted by the extracted $k_{\text{NO}_2^*-\text{S}}$, $k_{\text{NO}_2^*-\text{S}}$, and $k_{\text{NO}_2-\text{S}}$ values at 295 K. The quality of the fit is shown in Figure 3 with HNO₃ pressure of 30 mTorr in the surface-study cell.

The temporal absorption profiles from the photolysis of HNO₃ adsorbed on fused silica surfaces are compared to the temporal absorption profiles from the gas phase HNO₃ photolysis. As described in the previous publication of our group, [11] the temporal absorption profile at 552.84 nm following the gas phase photolysis of HNO₃ in the 0.5-1.5 Torr pressure range displayed an absorption maximum at 15 µs after the photolysis pulse, showed decrease in absorption with delay time in the 15-100 µs range due to the quenching of the excited NO₂ (with rate constant of $1.8 \times 10^4 \text{ s}^{-1}$) and the reaction between the excited NO₂ and HNO₃ to form an NO₂·HNO₃ adduct (with rate constant of 1.1×10^{-13} cm³ molecule⁻¹ s⁻¹), and the absorption value is nearly independent of time at delay times in the 150-400 µs range. In that study, we did not obtain absorption values at photolysis/probe laser delay of shorter than 15 µs because the PMT sometimes collected reflected photolysis beam inside the cell and we did not have a data analysis program that would reject photolysis pulse pick-up as ring-down curve at that time.

To find out whether temporal absorption at 552.84 nm from the gas phase HNO₃ photolysis also increases with delay time at $t < 15 \mu$ s similar to that observed from the photolysis of HNO₃ adsorbed on fused silica surfaces, we measured the temporal absorption profiles at 552.84 nm from the gas phase HNO₃ photolysis in this work and found that absorption also increases with delay time at $t < 15 \mu$ s. Thus, the excited NO₂ absorption increases with delay time at $t < 15 \mu$ s and decreases with delay time at $t > 15 \mu$ s following the gas phase HNO₃ photolysis suggesting that the excited NO₂ we observed at 552.84 nm was fed from another excited state of NO₂. The 308 nm photolysis of gas phase (or adsorbed) HNO₃ directly leads to the formation of the electronically-excited NO₂. The excited NO₂ we monitored in the 551.50–558.00 nm region

following the HNO₃ photolysis is that of the electronically-excited NO_2 that has undergone some degree of relaxation.

The temporal absorption profile at 552.84 nm from the photolysis of HNO₃ adsorbed on fused silica surfaces is also compared to the temporal absorption profile at this wavelength from the photolysis of HNO₃ adsorbed on Al surfaces and on ice films [11]. A different cell configuration was used to study the photolysis of HNO₃ on Al surfaces and on ice films. In that study, the surface photolysis temporal absorption profile showed an absorption maximum [11] at photolysis/probe laser delay of ~30 µs since the surface photolysis generated excited NO₂ needed to travel to the center of the cell to be detected by cavity ring-down spectroscopy.

The average excited NO₂ quantum yields from 308 to 351 nm photolysis of HNO_3 adsorbed on fused silica surfaces at 295 K were derived from the ratio of the number of excited NO₂ formed from the photolysis of adsorbed HNO_3 in the surface area where the photolysis and the probe laser overlapped to the number of photolysis photons absorbed by adsorbed HNO_3 in the same area.

The number of photolysis photons absorbed by surface-adsorbed HNO₃ ($N_{\rm abs,photon}$) in the photolysis/probe laser overlap area on each window was determined from (i) the photolysis beam energy striking on each fused silica Brewster window ($E_{\rm photolysis}$), (ii) the individual photon energy (hc/λ) at the photolysis wavelength (λ), (iii) the absorption cross section of the surface-adsorbed HNO₃ at the photolysis wavelength ($\sigma_{\rm HNO_3,surf}$), (iv) the surface concentration of HNO₃ ($n_{\rm HNO_3,surf}$), and (v) the ratio of probe beam area to photolysis beam area on each fused silica Brewster window ($A_{\rm probe}/A_{\rm photolysis}$), via the equation:

$$\begin{split} N_{\rm abs,photon} &= E_{\rm photolysis} \times \sigma_{\rm HNO_{3,surf}} \times n_{\rm HNO_{3,surf}} \times (A_{\rm probe}/A_{\rm photolysis}) \\ &\times 2/(hc/\lambda) \end{split}$$
(5)

The incident photolysis beam energy entering the cell was measured by a calibrated Joulemeter placed in front of the cell prior to its entrance through one front cell window. Once the photolysis beam entered the surface-study cell (Figure 1) through a fused silica window at the front side, it subsequently struck a fused silica Brewster window, before it exited the cell through a fused silica window on the back side. The photolysis beam energy striking on each fused silica Brewster window was corrected for photolysis beam transmission loss at the front cell window, and for reflection of the photolysis beam from the exit cell window. The absorption cross sections of HNO₃ adsorbed on fused silica surfaces at 308 and 351 nm were previously determined [8,9] by our group using Brewster angle cavity ring-down spectroscopy. They are 1.2×10^{-18} and 1.6×10^{-19} cm² molecule⁻¹ at 308 and 351 nm, respectively. Previous measurements [8,9] of the absorption of the probe laser beam by adsorbed HNO₃ on fused silica surfaces as a function of HNO₃ pressure in the cell by our group indicates that saturation of monolayer adsorption sites on fused silica surfaces occurred at HNO₃ pressures of about 14 ± 2 mTorr inside the cell. The maximum HNO₃ surface concentration to form monolayer adsorption on fused silica surfaces can be estimated using a van der Waals radius [21] of 5.5 Å for HNO3. It was about 1.1×10^{14} molecule cm⁻². Assuming the surface concentration of HNO₃ varies linearly with HNO₃ pressure in the cell over the 6–14 mTorr range, we can estimate HNO₃ surface concentration before the saturation of monolayer surface sites.

The number of the excited NO₂ molecules generated from 308 to 351 nm photolysis of adsorbed HNO₃ per window for a given HNO₃ pressure inside the surface-study cell were obtained from the measurements of the round-trip absorption by excited NO₂ at 552.84 nm at a photolysis laser-probe laser delay of 15 µs, the absorption cross section of the excited NO₂ on surface $\sigma_{\text{NO}_{2,\text{surf}}^{\dagger}}$ at 552.84 nm, and the size of the area (A_{probe}) where the photolysis and the probe beam overlapped, via $N_{\text{NO}_{2}^{\dagger}}$ = Absorption*

 $\textit{A}_{probe}/(4\sigma_{NO_{2,surf}^{\dagger}}).$ The absorption cross section of the excited NO₂ at 552.84 nm on surfaces is assumed to be similar to the cross section value [11] of the excited NO₂ in the gas phase $(9.4 \times 10^{-19} \text{ cm}^2 \text{ mol})$ ecule⁻¹). Shown in Figure 4 is round-trip absorption by excited NO₂ generated from the 308 nm photolysis of HNO₃ adsorbed on fused silica surfaces measured as a function of HNO₃ pressure in the surface-study cell at 295 K. As seen from Figure 4, the excited NO₂ absorption increased with increasing HNO₃ pressure up to HNO₃ pressure of about 10 mTorr inside the surface-study cell, the excited NO₂ absorption reached a plateau with HNO₃ pressures of about 12-14 mTorr in the surface study cell, and the excited NO₂ absorption showed further increase with increasing HNO₃ pressure for HNO₃ pressures higher than 16 mTorr. The plateau in the excited NO₂ absorption versus P(HNO₃) plot likely corresponds to absorption by excited NO₂ at steady-state concentration which was formed from the photolysis of adsorbed HNO₃ at saturation monolayer coverage. A plot similar to Figure 4 was obtained from the photolysis of adsorbed HNO₃ at 351 nm.

The excited NO₂ quantum yields from 308 to 351 nm photolysis of HNO3 adsorbed on fused silica surfaces were determined as a function of HNO₃ pressure in the surface-study cell in the 6-14 mTorr range. The excited NO₂ guantum yields were found to be independent of HNO₃ pressure in the 6–14 mTorr range to within experimental measurement uncertainty. The average excited NO₂ quantum yields from 308 to 351 nm photolysis of HNO₃ adsorbed on fused silica surfaces are 1.1 ± 0.2 and 1.0 ± 0.3 , respectively, where errors quoted (1σ) represent measurement precision. Our group previously obtained [11] the excited NO₂ quantum yields of 0.80 ± 0.15 and 0.92 ± 0.26 from the 308 nm photolysis of HNO₃ on Al surface at 295 and 253 K, and an excited NO₂ quantum yield of 0.60 ± 0.34 from 308 nm photolysis of HNO₃ on ice film at 253 K. The excited NO₂ quantum yield from the HNO₃ photolysis on fused silica surface obtained here is similar to those obtained from the HNO₃ photolysis on Al surfaces at 308 nm after considering combined uncertainties of both measurements. The excited NO₂ quantum yield from the HNO₃ photolysis on fused silica surface is higher than that from the HNO₃ photolysis on ice film possibly due to some degree of salvation of the excited NO_2 by ice.

3.2. Quenching/reaction rate constant of excited NO_2 with H_2O at 295 K

The quenching/reaction rate constant of the excited NO_2 and water vapor was determined by first introducing HNO_3 into the

Figure 4. The NO $_2^{\dagger}$ round-trip absorption measured at 552.84 nm from the 308 nm photolysis of adsorbed HNO₃ plotted as a function of HNO₃ pressure in the surface-study cell. The photolysis/probe laser delay was set at 15 μ s.

surface-study cell and depositing HNO₃ on fused silica Brewster window surfaces, and then introducing water vapor into the surface-study cell. Once the 308 nm photolysis beam struck on the fused silica Brewster window surfaces, the excited NO₂ generated from the photolysis of the adsorbed HNO₃ could either react with water vapor or be quenched by water vapor.

$$NO_2^{\dagger} + H_2O \rightarrow HONO + OH$$
 (6)

$$\mathrm{NO}_2^{\dagger} + \mathrm{H}_2\mathrm{O} \to \mathrm{NO}_2 + \mathrm{H}_2\mathrm{O} \tag{7}$$

The total rate constant for the quenching/reaction of the excited NO₂ with H₂O can be determined by measuring the pseudo-first order disappearance rate constants of the excited NO₂ in the presence of varying excess H₂O concentrations. The pseudo-first order disappearance rate constant of the excited NO₂ at a given excess H₂O vapor concentration can be determined by tuning the probe laser wavelength to the excited NO₂ absorption maximum at 552.84 nm and measuring the probe laser absorption as a function of time delay between the firing of the photolysis and the probe laser. The bimolecular rate constant for the reaction/deactivation of the excited NO_2 with H_2O is $(2.9\pm0.7)\times10^{-13}\,cm^3$ molecules⁻¹ s⁻¹ at 295 K, where error quoted represents 1σ measurement uncertainty. Due to the absorption of the ring-down probe beam by water vapor at 552.84 nm, the range of excess water vapor pressure that can be varied was limited in the current study. Thus, the water vapor pressure inside the cell was kept at 1.0 Torr and lower, and the NO_2^{\dagger}/H_2O rate constant measurement was subject to significant uncertainty.

Li et al. [22] reported the generation of OH radical from the reaction of the electronically-excited NO₂ with water vapor, H₂O, using laser induced fluorescence technique. In that study, the electronically-excited NO₂ was formed by exciting the ground state NO₂ with a visible light source. Li et al. monitored OH formation rates in the presence of varying excess H₂O concentrations and obtained a rate constant [22] on the order of $(1.7 \pm 0.8) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹. The rate constant between the electronically-excited NO₂ and H₂O obtained by Li et al. agrees with our NO[†]₂/H₂O reaction/deactivation rate constant within the combined measurement uncertainty of both studies.

4. Conclusions

In this Letter, we have investigated the 308 and 351 nm photolysis of HNO₃ adsorbed on fused silica surfaces by combining excimer laser photolysis with Brewster angle cavity ring-down spectroscopy, and we obtained the excited NO₂ quantum yields from the photolysis of the adsorbed HNO₃ at both wavelengths. The surface photolysis study was conducted by doping a monolayer or several monolayers of adsorbed molecules on the Brewster window surfaces and then directly probing photolysis intermediates/ products that are retained on the surfaces. The sensitivity of combining laser photolysis with Brewster angle cavity ring-down spectroscopic probe to study photodissociation of surface-adsorbed molecules at low surface coverage is clearly demonstrated in the current study. Time-resolved probing of the excited NO₂ following the photolysis of adsorbed HNO3 also sheds light on the nature of the excited NO₂ formed from the HNO₃ photolysis. We also determined the reaction/deactivation rate constant between the excited NO₂ and H₂O.

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